

Treatment of cyanide by using the Mexican modification of the Merrill-Crowe process

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ABSTRACT

Cyanide consumption can be a major factor which contributes to operating cost for cyanidation. Also after extraction and recovery of precious metals substantial amounts of cyanide are delivered to tailings ponds which creates environmental problems due to the toxicity of cyanides. In this regard, the air-sparged hydrocyclone (ASH) has been used as a reactor for the treatment of cyanide solutions in two ways; first for cyanide recovery by acidulation using the Mexican modification of the Merrill-Crowe process and second for cyanide destruction by oxidation with the use of chlorine dioxide (ClO_2). In both cases excellent performance can be achieved using the high capacity ASH technology.

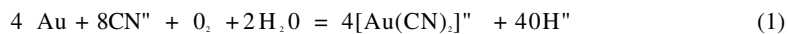
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INTRODUCTION

A variety of industrial effluents are known to contain cyanides. These various waste streams arise from different process industries such as those wastes from manufacturing synthetic fiber (acrylonitrile), coal conversion wastes or coking effluents (from the iron and steel industries), electroplating waste, petrochemical wastes, automobile industry waste (from plating shops) and wastes from the processing of precious metals resources by cyanidation. All these wastes have varied characteristics and are therefore subject to different processing and treatment strategies that depend upon the concentration of cyanides and the flow rate of the waste stream.

In mining operations, cyanidation is the predominant method by which gold and silver are recovered from their ores. In practice, the dissolution of gold and silver in aqueous cyanide solution is typically carried out with 0.03-0.3% NaCN, a pH greater than 10, and aeration to keep the pulp or solution saturated with oxygen (>7ppm). The overall reaction for the dissolution of gold and silver in dilute, aerated, alkaline cyanide solutions may be expressed by the Eisner equation



In this reaction oxygen is the oxidant and cyanide ion is the complexing agent or ligand. The reaction with silver is similar. However, the silver cyanide complex is weaker than the gold cyanide complex and stronger cyanide solutions and/or longer contact times must be employed for its dissolution.

After extraction and recovery of the precious metals substantial amounts of cyanide are delivered to tailings ponds which creates environmental problems due to the toxicity of cyanides. Thus, frequently it is necessary to recover or destroy cyanide from such solutions before recycle or discharge.

Due to the widespread use of cyanide in mining operations the recovery and destruction of cyanide is important both from the environmental aspects of wastewater and effluent treatment, and from the economic aspects associated with, in some cases, the high reagent consumption by the process itself. This was the case for a cyanidation process developed at Bads mine for the recovery of gold and silver from a pyrite concentrate⁽²⁾. The process comprises the following steps: leaching the complex sulfide concentrate by a one stage pressure oxidation in a high alkaline cyanide solution (1% cyanide), filtration and washing to separate the solid, and precipitation of gold and silver with zinc dust from the filtrate. The formation of metal cyanide complexes (copper, iron and zinc) with thiocyanate during pressure leaching results in species which are particularly toxic, because ultraviolet light decomposes thiocyanate to form cyanide, and it is then possible that sun light may liberate cyanide which would be toxic to aquatic life. Also the moderate cyano-complexes can be

readily decomposed by acidification or oxidation. In view of these considerations cyanide recovery or destruction is a necessary processing step-

To reduce the cyanide level for disposal (<0.02 mg/l), several cyanide treatment systems have been developed. All these methods are based on cyanide recovery by acidulation and/or destruction by chemical oxidation¹¹. In many cases the process is burdened with high reagent costs and royalty payments¹¹. In this regard, two applications of the air sparged hydrocyclone are considered for the treatment of cyanide solutions: recovery, acidulation using the Mexican modification of the Merrill-Crowe process¹² and destruction, chemical oxidation with the use of chlorine dioxide (ClO_2) which has not been reported previously. Both methods are examined using the air-sparged hydrocyclone technology (ASH), which allows for intimate contact between the cyanide solution and gas at a high specific capacity.

Air-Sparged Hydrocyclone Technology

The air-sparged hydrocyclone (ASH) technology was originally developed at the University of Utah for fast and efficient flotation of fine particles^{13,14}. Recent studies indicate that the fluid flow conditions inside the ASH system can be effectively exploited for air stripping of VOCs from contaminated water¹⁵

The ASH unit consists of two concentric right-vertical tubes and a conventional cyclone header at the top. The porous inner tube is constructed of any suitable material such as plastic, ceramic, or stainless steel and allows for the sparging of air or any other gas or steam. The outer nonporous tube serves to establish an air jacket and provide for the even distribution of the air through the porous tube. Thus the ASH can be used for air stripping where volatile species such as HCN that volatilizes as a gas (Henry's law of constant of 6.4 atm/mole)¹⁶ can be displaced from solution by air or for chemical oxidation. In this case the destruction of cyanide can be achieved with an oxidizing gas such as ClO_2 .

The cyanide solution is fed tangentially at the top through the cyclone header to develop a swirl flow adjacent to the inside surface of the porous tube, leaving an empty air core centered on the axis of the ASH unit. The high-velocity swirl flow shears the sparged air to produce a high concentration of small bubbles and intimate interaction between these numerous fine bubbles and the cyanide solution. Gaseous products are then transported radially to the center of the cyclone. The major portions of the gas phase moves towards the vortex finder of the cyclone header, and is vented into an appropriate post-treatment device. The specific capacity of the ASH system is at least 300-400 gallons per minute per cubic foot of cell volume, 100-600 times that of conventional air-stripping equipment. The ASH equipment requires an operating space significantly less than a packed tower or other gas contacting equipment, resulting in a significant savings in capital cost. A schematic drawing of the ASH unit as used for the case of air stripping of cyanide is presented in Figure 1.

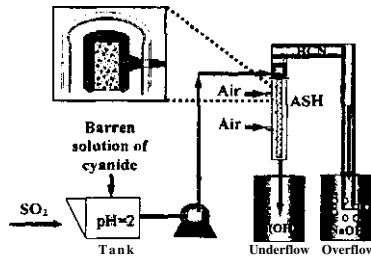


Figure 1. Schematic drawing of the Air-Sparged Stripping Technology.

Cyanide Recovery

Free cyanide exists as the uncomplexed cyanide ion, CN^- , and molecular hydrogen cyanide, HCN . These species are related by the acid dissociation of HCN :



The concentration of free cyanide is the sum of the CN^- and HCN concentrations, and the distribution is illustrated by the equilibrium diagram shown in Figure 2. This figure shows the proportions of free cyanide as CN^- and HCN as a function of pH at 25°C . At pH values above 9.2 CN^- predominates, and at pH values below 9.2 HCN predominates.

Hydrogen cyanide (HCN), also known as hydrocyanic acid, is a colorless gas or liquid with a boiling point of 25.7°C , a vapor pressure of 100 KPa at 26°C and Henry's law constant of $6.4 \text{ atm/mole}^{(1)}$.

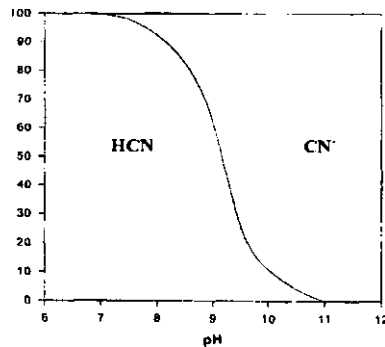


Figure 2. Equilibrium distribution diagram for free cyanide versus pH.

In addition to free cyanide other complexes such as the metal cyanide complexes formed with gold, mercury, zinc, cadmium, silver, copper, nickel, iron and cobalt must be considered. These are classified into five general categories, as shown in Table 1⁽¹⁰⁾.

Table 1. Classification of cyanide and cyanide complexes on the basis of stability

Classification	Compound
Free cyanide	CN ⁻ , HCN
Simple compounds	
a) readily soluble	NaCN, KCN, Ca(CN) ₂ , Hg(CN) ₂
b) neutral insoluble salts	Zn(CN) ₂ , Cd(CN) ₂ , CuCN, Ni(CN) ₂ , AgCN
Weak complexes	Zn(CN) ₄ ⁻² , Cd(CN) ₄ ⁻² , Cd(CN) ₃ ⁻¹ ,
Moderately strong complexes	Cu(CN) ₂ ⁻ , Cu(CN) ₃ ⁻² , Ni(CN) ₄ ⁻² , Ag(CN) ₂ ⁻
Strong complexes	Fe(CN) ₆ ⁻⁴ , Co(CN) ₆ ⁻⁴ , Au(CN) ₂ ⁻ , Fe(CN) ₆ ⁻³

The cyanide recovery process utilizes the volatility of HCN at a lowered pH to strip free cyanide from solution or slurry and recover it in a caustic solution. It has been almost 80 years since the Merrill-Crowe process for cyanide regeneration was developed by the Compañía Beneficiadora de Pachuca, Mexico (British Patent No. 241669, 3.9.24)⁽⁵⁾ and until today no significant changes to the process have been made. The process involves acidifying clarified solution, then stripping the HCN formed and reabsorbing it from the air stream with a caustic or milk of lime spray.

Today, the company⁽¹⁰⁾ acidifies the clarified cyanide solution with sulfuric and hydrochloric acids (to avoid gypsum formation). In the volatilization stage a series of four stripping towers packed with wooden grids are used. The towers are constructed of 316 stainless steel and measure about 95 cm of diameter x 5 m in height. A total cyanide recovery of about 95 % is achieved with about 50 percent removal realized in each of the four stripping stages.

Experimental Procedure

Experiments for cyanide recovery by air stripping, at the Saltillo Institute Technology pilot plant included preparation of the barren solution with SO₂ gas (pH=2) for HCN formation, and stripping with a 2-inch diameter ASH unit. Chemical analysis for cyanide in the effluent streams was accomplished with a reflux distillation method. The cyanide so collected was quantified by titrimetric and/or the ion selective electrode technique.

During experiments two streams had to be delivered to the ASH: cyanide solution and air. Cyanide solution was provided by a sump pump mounted on a 300 liter retention tank. The

cyanide solution flowrate was adjusted using a regulated return flow to the tank. Using an air compressor, air flow was evenly distributed between the upper and lower sections of ASH and all parts were sealed with gaskets. Cyanide solution acidified to pH=2 in the tank was fed at different flowrates to the top of the ASH. The exit pipe was located at the bottom of the closed regenerated cyanide tank to prevent release of HCN. The HCN laden air was collected in the absorber where reaction with caustic 10% regenerated the NaCN solution. Operators were provided with personal HCN gas monitor/alarm units.

RESULTS AND DISCUSSION

Experiments were performed using 250 ppm of CN^- prepared from plant at ambient temperature (24 °C). These tests indicated that stripping and regeneration of cyanide is pH dependent. As seen in Figure 3, the pH, and solution flowrate influence cyanide recovery. Thus at a low pH value when the concentration of CN^- is very small, a high recovery is achieved due to the easy volatilization of HCN. On the other hand at pH=5 the recovery is significant lower (52% at 20 l/min).

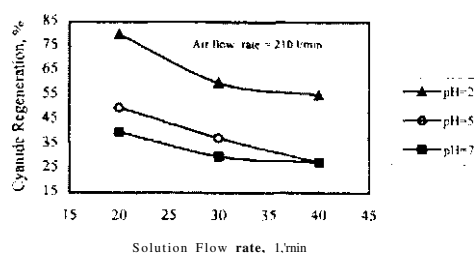


Figure 3. Cyanide regeneration with ASH.

Based on these preliminary test results, an initial economic comparison with current Merrill-Crowe processes⁽⁵⁾ is summarized in Table 2. All of these processes for cyanide recovery are current versions of the original Merrill-Crowe process⁽⁵⁾.

Finally in Table 3, based on the pilot plant results, estimates of the cost of cyanide recovery have been prepared per kilogram of cyanide recovery and the performance of the ASH compares favorably to the packed tower technology.

Table 2. Comparison of the results for Merrill-Crowe processes

Mine	Reactor	Air/Liq	% Rec.	CN _{IN}	CN _{OUT}	Streams
Flin Flon Mine	4 towers	521	92	560	44	Solution
Real del Monte Mex.)	4 towers	340	93	220	3	Solution
AVR (Canmet)	4 towers	330	99	330	2	Solution
C.R.P. (Tasmania)	-	-	99	200	5	Solution
Cyanisorb (Cyprus Minerals)	4 towers	-	99	600	30	Slurry
Ash (Bacis. Mexico)	1 ASH	10	80	250	50	Solution
Ash (Bacis. Mexico)	1 ASH	100	90	250	25	Slurry

Table 3. Comparison of cost and performance

Mine	Cost (US \$/kg CN)	Ratio Air/solution	% Recovery Single stage	Remarks
Real del Monte (packed tower)	1.00	200-350	64	Build-up gypsum and copper thiocyanates precipitates
Bacis Mine (ASH)	0.85	20- 100	80	Free of precipitates

The advantage of the ASH technology over packed towers is the residence time. In packed towers the residence time for stripping varies from 7 to 20 minutes whereas the ASH operates with a time of only 4 seconds⁽⁸⁾.

Cyanide Destruction

The leading processes currently being applied for the cyanide destruction from effluents is based on the oxidation of cyanide and include alkaline chlorination, hydrogen peroxide, INCO/SO₂ air process, ozone and biological treatment. All these methods have distinct advantages and disadvantages as outlined in Table 4^(3,13).

Table 4. Advantages and disadvantages of various cyanide destruction options ^(3,13)

Detoxification method	Advantages	Disadvantages	Suitability for		Decomposes	
			Low CN ¹	High CN ¹¹	SCN	FeCCN ¹²
Alkaline Chlorination	Technology well established	Adds potentially objectionable cations / anions to water Excess hypochlorite is toxic Chlorine can react with organics to form chlorinated compounds Poor process control results in toxic intermediates Reacts preferentially with Thiocyanate Many of the less expensive Hypochlorite sources require Special handling				
Hydrogen Peroxide	Excess reagent decomposes to water an oxygen Relatively simple to operate Not as reactive with thiocyanate	Reagent cost If precipitating ferrocyanides with copper, must dispose of precipitate				
S ₂ /Air (INCO) Process	Reagent is very inexpensive	At least some of reagent savings are offset by license/royalty payments Process adds sulfates to treated water If precipitating ferrocyanides with copper, must dispose of precipitate				
Biological Oxidation	"Natural approach" received well publicly, and by regulators Uses heaps as a reactor, reducing total wash volumes, and possibly reach low flow areas of the heap more effectively Relatively inexpensive Can treat total cyanides without generating another waste stream	Technology is not well established Requires combination of metallurgy, biology and process engineering Tends to be very site specific, with each ore type requiring a specific evaluation and study				
Ozonation	Some regeneration of cyanide possible	Cost of ozone equipment Reagent cost	**	**	* ¹	X

From Table 4 it is noted that none of these processes for the detoxification of cyanidation effluents use chlorine dioxide (ClO_2).

The properties of chlorine dioxide, like those of chlorine, must necessarily be considered both in the gas phase and in the aqueous phase⁽¹⁴⁾. Chlorine dioxide is almost never used commercially as a gas because of its explosiveness. For potable water and wastewater treatment process, it is only used in aqueous solutions. One of the important physical properties of chlorine dioxide is its high solubility in water, particularly chilled water. Since it is about ten times more soluble than chlorine, this difference in solubility provides a practical means of separating the two gases in the manufacturing process. Paradoxically, it is extremely volatile and can be easily removed from dilute aqueous solution by air stripping.

Although chlorine dioxide is soluble in water, it does not react chemically with water as does chlorine. It is unstable gas and must be generated on site. For the purpose of comparison, the common oxidants used for cyanide destruction are summarized in Table 5, together with their half cell potentials. For convenience, each oxidant can be expressed in terms of free reactive oxygen, $[\text{O}]^1$.

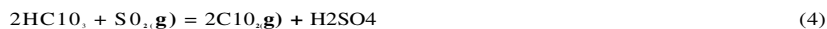
Table 5. Oxidants, half-cell reactions and standard potentials for common oxidants^(14,15).

	Half reaction	Conditions	E° , volts	Equivalent Reactive Oxygen
Oxidant				Moles $[\text{O}]$ per Mole Oxidant
O_3	$\text{O}_3 = [\text{O}] + \text{O}_2$	Acidic	2.07	1.0
		Basic	1.25	
ClO_2	$2\text{ClO}_2 + \text{H}_2\text{O} = 5[\text{O}] + 2\text{Cl}^- + 2\text{H}^+$	Acidic	1.95	2.5
		Basic	1.16	
H_2O_2	$\text{H}_2\text{O}_2 = [\text{O}] + \text{H}_2\text{O}$	Acidic	1.72	1.0
HOCl	$\text{HOCl} = [\text{O}] + \text{Cl}^- + 2\text{H}^+$	Acidic	1.49	1.0
		Basic	0.89	
Cl_2	$\text{Cl}_2 + \text{H}_2\text{O} = 2\text{Cl}^- + 2\text{H}^+ + [\text{O}]$	Acidic	1.36	0.5
K_2FeO_4	$2\text{FeO}_4^{2-} + 2\text{H}_2\text{O} = 3[\text{O}] + \text{Fe}_2\text{O}_3 + 4\text{OH}^-$		0.74	1.5
		Acidic	2.20	
		Basic		
Reductants				
SO_2	$\text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^- = \text{SO}_3^{2-} + 2\text{OH}^-$	Acidic	0.93	

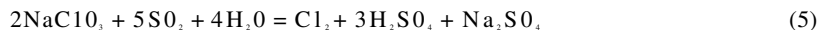
Based on the data in this Table, it is evident that chlorine dioxide (ClO_2) provides the highest free reactive oxygen, $[\text{O}]$, and also the highest oxidant strength compared to other common oxidants for cyanide destruction. The objective of this research to examine the use of ClO_2 for cyanide destruction using the ASH technology.

Experimental Procedure

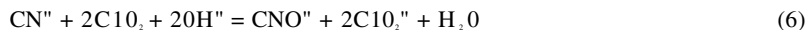
The method used for generating on-site ClO_2 consists of blending a 45 % solution of sodium chlorate with 66°Be sulfuric acid in the top of a reaction vessel. Air containing 10 % SO_2 is blown into a diffuser at the bottom of this vessel and chlorine dioxide plus air is extracted at the top of the vessel (chlorine dioxide content is between 6-10 percent), the so-called Mathieson process^(16,17). The basic reactions are:



Side reactions also take place, including:



The exit gases are reacted with the cyanide solution in the Air-Sparged Hydrocyclone where the oxidation or destruction of cyanide is expected to occur according to the following reaction:



The equipment and experimental set-up are similar to that describes previously (Figure 1).

Results and Discussion

One of the primary process variables for cyanide destruction with ClO_2 is the pH of the solution. Table 6 shows the results of a set of experiments for the effect of pH on cyanide destruction. The effluent cyanide concentration (both free, CN_{FREE} , and combined, CN_x) is plotted as a function of pH in Figure 4. It is evident that free cyanide is destroyed at all pH values. The combined cyanide CN_x , is destroyed most effectively at high pH values.

Table 6. Effect of pH on cyanide destruction.

Feed solution = 250 mg/L total cyanide.

Solution flowrate = 40 L/min.

Gas (6% ClO_2) flowrate = 1.00 L/min.

Cyanide solution (mg/l)		Final effluent (mg/l)		% Destruction	
pH	CNTOT	CNFREE	CN _x	CNFREE	CN _x
11.23	250	0.12	52.54	99.9	78.8
9.20	250	0.19	103.0	99.9	58.8
2.57	250	0.11	187.0	99.9	25.2

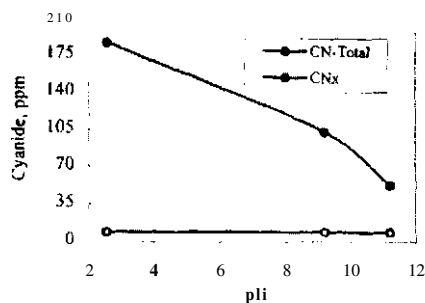
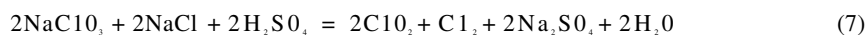
CN_x = CNO\ HCNO, Fe(CN)₆⁴⁻, etc.

Figure 4. Effect of pH in cyanide destruction.

Effect of NaCl. These experiments consist in the elimination of the use of sulfur dioxide (SO_2) for the chlorine dioxide generation. The basic reaction of this process is:



Air is blown into the bottom of the vessel driving off the gas formed which is diluted by the incoming air. Then the mixture of ClO_2/Cl_2 is circulated through the ASH. The data are presented in Table 7. The results show 99.9% destruction of free cyanide and the behavior is similar that when sulfur dioxide (SO_2) was used for chlorine dioxide generation.

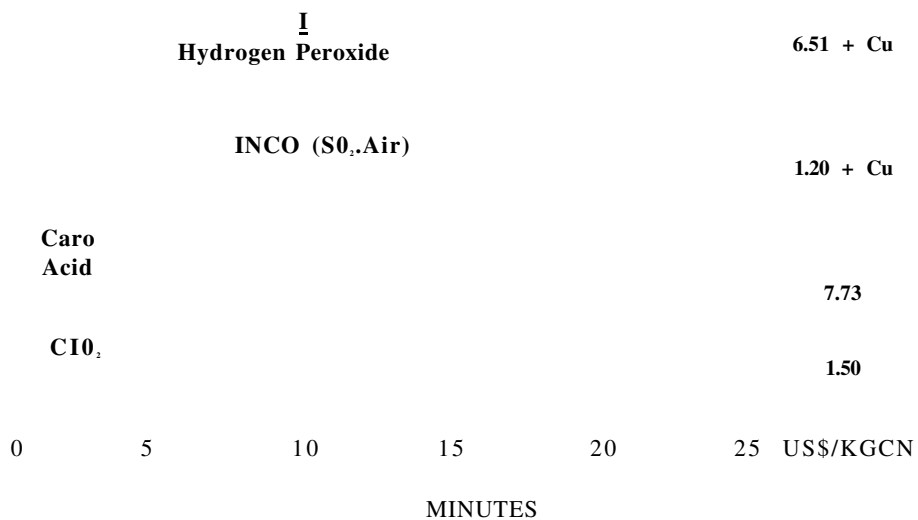
Feed solution = 250 mg/L total cyanide.
Solution flowrate = 40 L/min.
Gas (C10₂/C1₂) flowrate = 100 L/min.
pH = 11.2

Barren bleed (mg/L)		Final effluent (mg/L)		% Removal	
NaCl(g/l)	CNTOT	CNFREE	C N _x	CNFREE	C N _x
1.23	250	0.02	52.54	99.9	78.8
0.80	250	0.10	149.0	99.9	40.4
0.40	250	0.09	193.0	99.9	22.8
0	250	0.10	222.0	99.9	11.2

$$\text{CN}_x = \text{CNO}^-, \text{HCNO}, \text{Fe}(\text{CN})_6, \text{ etc.}$$

A summary of the comparison of the reaction times and costs of cyanide destruction are presentes in Table 8.

Table 8. Comparison of the reaction times and costs of cyanide destruction¹⁸¹.



CONCLUSIONS

Cyanide recovery process with the ASH solves the problem in an economically and environmentally acceptable manner. The ASH with the chlorine dioxide has been proven in bench and pilot plant scale applications and has been proven effective in the treatment of cyanide from solution and slurries. The economics of the process are quite attractive.

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